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A novel biodiesel production method consisting of oil extraction and transesterification from wet microalgae

Ching-Lung Chen[a], Jo-Shu Change[a,b,c*], Chien-Chang Huang[d], Kao-Chia Ho[a], Ping-Xuan Hsiao[a], Meng-Shan Wu[a]

[a]*Department of Chemical Engineering, National Cheng Kung University, Tainan, Taiwan*
[b]*Center for Biosciences and Biotechnology, National Cheng Kung University, Tainan, Taiwan*
[c]*Research Center for Energy Technology and Strategy, National Cheng Kung University, Tainan, Taiwan*
[d]*Department of Cosmetic Science, Providence University, Taichung, Taiwan*

Abstract

Microalgae biodiesel is one of the most promising alternatives to fossil fuels. However, how to quickly and cost-effectively obtain a large quantity of oil form microalgae is always a challenge. In this study, a novel method was developed for biodiesel production. This method was composed of microwave disruption, partial water removal, oil extraction and transesterification. The wet microalgal biomass with a moisture content of about 80 wt% was used as the feedstock for biodiesel production. The results show that the moisture of the wet microalgae after microwave disruption and partial water removal decreased to nearly 50 wt%. The oil recovery in oil extraction from the pretreated microalgae was over 90%, and the conversion in transesterification was higher than 90%. Moreover, the test for the large amount of microalgae sludge (400 g) shows that this method was suitable for the use in large-scale microalgae-based biodiesel production.

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Keywords: Wet microalgae, biodiesel production, microwave disruption, oil extraction, transesterification

1. Introduction

Biodiesel is one of the most promising alternatives to fossil fuels because it has many advantages such as high flash point, high lubricity, high biodegradability, and can be used in conventional compression-ignition engines without any modification [1]. Moreover, microalgae have the advantages of high growth rates, short maturity period, high biomass production rates, low environmental impacts [2], and no competition with crops in arable lands. Therefore, microalgae are better feedstocks over the traditional resources, such as soybean oil and sunflower oil, which all seriously compete with food crops [3].

* Corresponding author. Tel.: +886-275-7575#62651; fax: +886-234-4496.
E-mail address: changjs@mail.ncku.edu.tw

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Conventional process for oil extraction from microalgae consists of the microalgae harvesting, biomass drying and oil extraction [4], but the drying step is heavily energy intensive. Thus, more and more studies are focusing on using wet microalgae for oil extraction and biodiesel production [5-10]. However, the technologies, such as centrifugation and supercritical fluid extraction, used in these studies, have low commercial viability. Therefore, in this study, we developed economically and technologically feasible methods for microalgae biodiesel production from wet microalgae feedstock to establish commercialization and large-scale microalgae-based biodiesel production process.

2. Materials and methods

2.1 Materials

Both hexane (ACS) and sodium hydroxide (NaOH, ACS) were bought from Macron Fine Chemicals, and industrial methanol (>99%) was purchases from Uni Ward.

The microalgal strain *Chlorella vulgaris* ESP-31 was from University Center for Bioscience and Biotechnology, National Cheng Kung University, Tainan, Taiwan, and the culture conditions is described in Yeh et al. [11]. The microalgae biomass was collected with a continuous flow centrifuge at 13500 rpm, resulting in the production of the microalgae sludge with a moisture content of about 80%. Besides, the oil content in the microalgae was about 30% by weight of dry biomass.

2.2 Pretreatment

The procedures of the method developed in this study are indicated in Fig. 1. The first step was the pretreatment of microalgae sludge. In general, 100 g sludge was place in a customized container, which was modified from a 500 mL serum bottle, and mixed with 300 mL methanol at 400 rpm for 20 minutes with a magnetic stirring bar. The bottle was then moved into a microwave oven at 350W for 10 min for cell disruption. After that, the mixture was poured into a commercial filtration bag for nut milk, which was centrifuged with a spin dryer to removal liquid from the mixture to yield a microalgae cake.

2.3 Wet oil extraction

An appropriate amount (5 g) of the microalgae cake was place in a 100 mL serum bottle. Then, 10 mL methanol and 20, 30, 40, 50, and 60 mL of hexane were added into the flask to identify the suitable hexane-to-methanol ratio. Moreover, the extraction temperature of 25, 35, 45, 55, and 65^{o}C and the extraction time of 20, 40, 60, 80, 100, and 120 min were also tested to recover microalgae oil. After stirring at 600 rpm under the above-mentioned conditions, the mixture was centrifuged at 6000 rpm for 3 min to achieve the separation of oil phase, water phase, and microalgae residue. Then, the oil phase including microalgae oil and hexane was preserved in another 100 mL serum bottle. In order to calculate the oil recovery, 1 mL of the hexane solution was passed through the transesterification reaction at a hexane solution/methanol (containing 0.5 wt% NaOH) ratio of 2:1 at 65^{o}C and 600 rpm for 30 minutes.

2.4 Transesterification

The methanol containing 0.5 wt% NaOH was added into the serum bottle, which was filled with microalgal oil-containing hexane solution from the wet oil extraction, with different volume ratios of oil phase to methanol, such as 2:1, 4:1, 6:1, 8:1, and 10:1. In addition, the reaction temperature of 25, 35, 45, 55, and 65^{o}C and the extraction time of 5, 10, 15, 20, 25, and 30 minutes were used to find the best

conditions for biodiesel production. The transesterification reaction was performed at 600 rpm at the conditions mentioned above. After that, the mixture was centrifuged at 6000 rpm for 3 min and then the hexane solution passed through the vacuum distillation to yield pure biodiesel and recover pure hexane.

3. Results and discussion

A microalgae cake with a weight of about 40 g and a solid content of 50% was obtained after centrifuged with a spin dryer for clothes in the pre-treatment step. The cake was subjected to the wet oil extraction step, which was conducted at different extraction time, temperature and solvent ratio to obtain the optimal operating conditions for the recovery of microalgae oil. Other factors, such as the use of a cooling system for the recovery of hexane vapor and energy consumption, were also investigated. Fig. 2 shows the effects of the extraction time, the ratio of hexane to methanol, and the extraction temperature on the microalgae oil recovery. The results show that at room temperature (25^{o}C), the oil recovery increased with an increase in the extraction time and the recovery reached plateau starting at 80 min. The suitable extraction temperature was 55^{o}C. Under these conditions, a cooling system should be used to for safety reason due to serious hexane evaporation. The increase in the ratio of hexane to methanol could also increase the oil recovery, and the recovery was over 95% when the hexane/methanol ratio was 3:1 (30 mL:10 mL). Hence, the best conditions for the wet oil extraction from the microalgae cake were extraction time, 80 min; extraction temperature, 45^{o}C; the hexane/methanol ratio, 3:1.

In the transesterification step, the factors considered were the reaction temperature, the hexane solution/methanol ratio, and the reaction time. As shown in Fig. 3, the best temperature was 45^{o}C, at which the conversion was over 95%. The suitable ratio of hexane solution to methanol with 0.5 wt% NaOH was 6:1, as the conversion at the ratio of 6:1 was higher than 95%. Moreover, the reaction time of 15 min was chosen because the conversion after 15 min reaction was higher than 95%.

About 400 g of microalgae sludge was used to exam the procedures developed and the operating factors identified in this study. Some operation details were changed in this study: (1) A mechanical stirrer at 270 rpm was used to substitute the magnetic stirring bar at 600 rpm; (2) The full amounts of microalgae sludge, microalgae cake and hexane solution containing microalgae oil were used in the corresponding steps, except the microwave disruption in which the sludge/methanol mixture was evenly divided into 4 batches to run the experiments separately; (3) The solid/liquid separation with a spin dryer and a filtration bag and the following oil/water phases separation by gravity were substituted for the centrifugation at 6000 rpm for 3 minutes. The results of this test show that the oil recovery and conversion were both over 90%, suggesting that the proposed procedures are suitable for the use in large-scale microalgae-based biodiesel production.

4. Conclusion

A novel biodiesel production method composed of the pre-treatment, oil extraction and transesterification using wet microalgae as feedstock was developed in this study. Under the optimal conditions, the microalgae oil recovery and biodiesel production were both over 90%. Furthermore, using a large amount of microalgae sludge as feedstock for biodiesel production is feasible using the proposed method, thus confirming that the proposed method has the potential to be used in large-scale operation.

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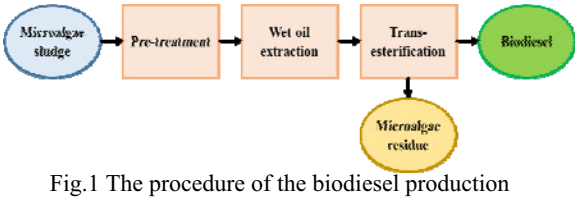

Fig.1 The procedure of the biodiesel production from wet microalgae

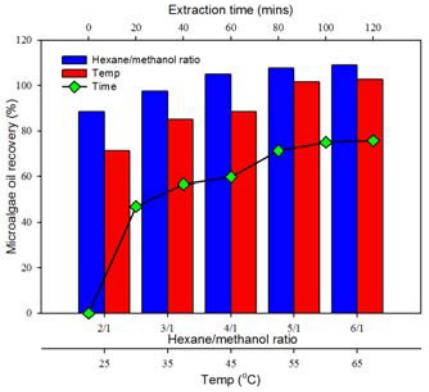

Fig. 2 The effects of the extraction time, temperature, and the hexane/methanol ratio on microalgal oil recovery

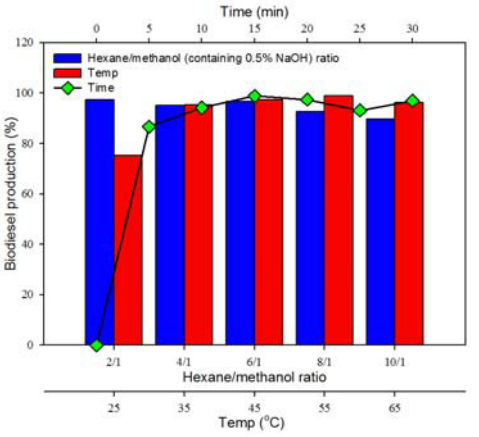

Fig. 3 The effects of the reaction temperature, the hexane solution/methanol ratio, and the reaction temperature on biodiesel production